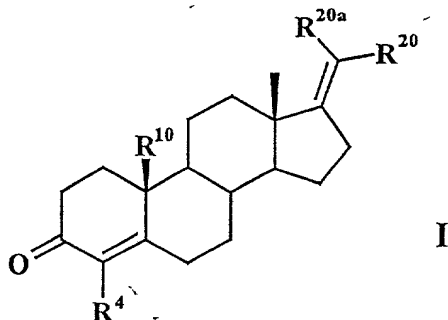


Claims

1. 17-Methylene steroids of general formula I



in which

R^4 stands for a halogen atom or a pseudohalogen,

R^{10} stands for a hydrogen atom or a straight-chain or branched C_1 - C_4 alkyl group,

R^{20} and R^{20a} , independently of one another, represent a hydrogen atom, a straight-chain or branched C_{1-4} alkyl or hydroxy- C_{1-4} alkyl group, or

one of radicals R^{20} and R^{20a} means a hydrogen atom, a straight-chain or branched C_{1-4} alkyl or hydroxy- C_{1-4} alkyl group, and the other radical means a halogen atom or a pseudohalogen.

2. 17-Methylene steroids according to claim 1, characterized in that R^4 stands for a chlorine or bromine atom or a cyano group.

3. 17-Methylene steroids according to claim 1 or 2, wherein one of radicals R^{20} and R^{20a} means a hydrogen atom or a methyl group, and the other radical means a fluorine, chlorine or bromine atom, an azido, cyano or rhodano group or hydroxymethyl.

4. 17-Methylene steroids according to claim 1, 2 or 3, wherein R^{10} stands for a hydrogen atom or a methyl group.

5. 17-Methylene steroids according to claim 1, namely

- 1) E-17-Chloromethylene-4-chloro-estr-4-en-3-one,
- 2) E-17-Cyanomethylene-4-chloro-estr-4-en-3-one,
- 3) Z-17-Cyanomethylene-4-chloro-estr-4-en-3-one,
- 4) Z-17-(1')-Cyanoethylidene-4-chloro-estr-4-en-3-one,
- 5) Z-17-Ethylidene-4-chloro-estr-4-en-3-one,
- 6) E-17-Ethylidene-4-chloro-estr-4-en-3-one,
- 7) E-17-Bromomethylene-4-chloro-estr-4-en-3-one,
- 8) Z-17-Chloroethylidene-4-chloro-estr-4-en-3-one,
- 9) Z-17-Bromoethylidene-4-chloro-estr-4-en-3-one,
- 10) E-17-Chloromethylene-4-cyano-androst-4-en-3-one,
- 11) E-17-Chloromethylene-4-chloro-androst-4-en-3-one,
- 12) E-17-(2')-Hydroxyethylidene-4-chloro-estr-4-en-3-

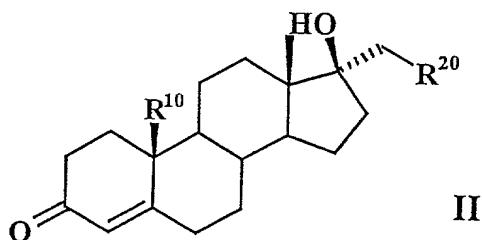
one and

- 13) Z-17-(2')-Hydroxyethylidene-4-chloro-estr-4-en-3-

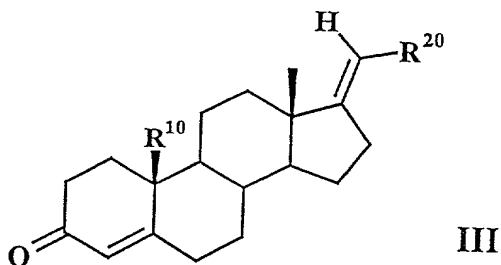
one.

10/25/00 09:59:56

6. Process for the production of 17-methylene steroids according to claim 1, in which R^{20a} means a hydrogen atom, wherein a compound of general formula II,

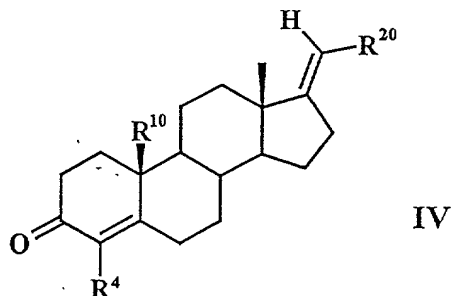


is reacted in an aprotic solvent with an acid chloride to a 17-methylene steroid of general formula III,



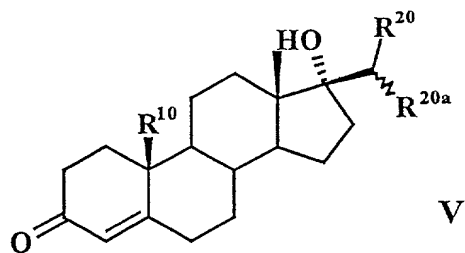
the 4,5-epoxide is generated with $H_2O_2/NaOH$, the 4,5-epoxide is then opened with a nucleophilic reagent, which is derived from a halogen atom or pseudohalogen, in a dipolar aprotic solvent to a halogen- or pseudohalogen hydrin, and optionally reacted with mineral acid, carboxylic acid or

sulfonic acid in a protic or aprotic solvent with dehydration to a compound of general formula IV, in which

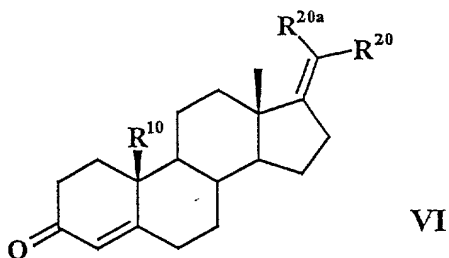


R^4 stands for a halogen atom or pseudohalogen, whereby R^{10} has the meaning indicated in claim 1, and R^{20} means a C_{1-4} alkyl or hydroxy- C_{1-4} alkyl group, a halogen atom or a pseudohalogen.

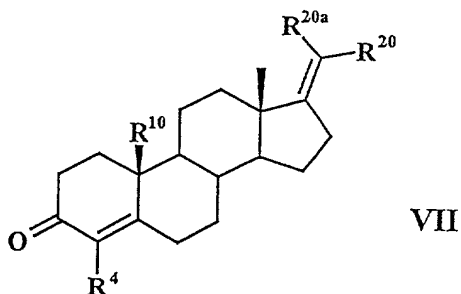
7. Process for the production of 17-methylene steroids according to claim 1, wherein a compound of general formula V,



is reacted with an acid chloride in an aprotic solvent to a methylene steroid of general formula VI,



the 4,5-epoxide is generated with $\text{H}_2\text{O}_2/\text{NaOH}$, the 4,5-epoxide is then opened with a nucleophilic reagent, which is derived from a halogen atom or pseudohalogen, in a dipolar aprotic solvent to a halogen- or pseudohalogen hydrin, and optionally reacted with mineral acid, carboxylic acid or sulfonic acid in a protic or aprotic solvent with dehydration to a compound of general formula VII,



in which R^4 stands for a halogen atom or pseudohalogen, whereby R^{10} has the meaning indicated in claim 1, and R^{20}

means a C₁₋₄ alkyl or hydroxy-C₁₋₄ alkyl group, and R^{20a} means a hydrogen atom, a halogen atom or a pseudohalogen.

8. Pharmaceutical compositions that contain at least one 17-methylene steroid according to claim 1, 2, 3, 4 or 5, optionally together with pharmaceutically compatible adjuvants and vehicles.

9. 17-Methylene steroids according to one of claims 1 to 5 for use as therapeutic active ingredients.

10. Use of the compounds according to one of claims 1 to 5 for treatment of prostate diseases, alopecia of the male type, acne and hirsutism, for contraception in men and women and/or for inhibition of 5 α -reductase.